The Use of Cellulose Sample for Material's Flammability and Pyrolysis Tests

M. DAIKOKU, S. VENKATESH AND K. SAITO

Combustion and Fire Research Laboratory
Dept. of Mechanical Engineering
University of Kentucky
Lexington, KY 40506-0108

(Received October 6, 1993)
(Revised January 5, 1994)

ABSTRACT: During transient pyrolysis tests of charring and non-charring materials, we noticed that sample preparation is crucial to obtain reliable data, on which theoretical models are based. Different researchers use different sample preparation techniques which some time causes disagreement in the results and create ambiguity when test results are compared. In this paper, we propose a bench mark sample preparation technique to clarify the experimental ambiguity and establish a reliable/common data base. Pyrolysis tests were performed by exposing PMMA, douglas-fir particle board (DFPB), and cellulose samples to external radiant heat using quartz and cone heaters. The cellulose sample is suggested for its homogeneity and combustion characteristics similar to natural wood in order to eliminate a variety of experimental uncertainties due to inhomogeneity of particle board and wood samples for use in pyrolysis tests. Temperatures were measured at the front and back surfaces and at other intermediate locations using fine thermocouples. Thermal conductivity of DFPB and cellulose was then approximated from the measured temperature distributions as the sum of a linear temperature dependent term and a radiation penetration effect into the pourous structure in the pre-lyrolysis zone. Effect of in-depth radiation absorption through the surface of the PMMA samples was estimated for various external radiant heat flux values; and it was found that in-depth radiation is an important factor in controlling the rate of heat transfer into the sample.

KEY WORDS: flammability test, cellulose sample, PMMA, effective thermal conductivity, in-depth radiation absorption, cone calorimeter.

0734-9041/94/05 0424-18 $06.00/0
© 1994 Technomic Publishing Co., Inc.

INTRODUCTION

STUDIES ON PYROLYSIS of commonly used building materials are important in fire research, particularly from the fire safety point of view. In the past numerous studies were conducted on this topic in both the U.S. and abroad and a number of papers have been published. A most successful model for a well defined ideal material with simple geometry was recently developed by Delichatsios [1,2]. Yet a simple and practically useful prediction model, applicable to many different building materials with different geometry, is not foreseeable in the near future due to the complexity of geometry in buildings and the vast variety of materials. The material's pyrolysis study is not exceptional, therefore, experiments still play a major role in investigating the pyrolysis problems. An excellent example is the careful and through experimental studies conducted by Kashiwagi et al. [3,4]. Thus, Emmons directs the future fire research by saying "Mature engineering fields base their work on fundamental laws of nature combined with well verified and correlated experimental data." (quoted from his seminar "The New Fire Engineering" given at the University of Kentucky, March 1992).

Transient pyrolysis tests were conducted for charring and non-charring materials in a 100% nitrogen environment using a quartz-heater pyrolysis-test apparatus developed by Alpert at Factory Mutual Research (FMR) [1]. Through summer scientist fellowship program, we participated in an FMR's fire research program on fuel pyrolysis project in the summer of 1988 and 1989. The program was coordinated by Ron Alpert as the managing director and John deRis as the advisor. Other participants include Mike Delichatsios, Mary Delichatsios, Mary Mathews, all from FMR and Shyam Venkatesh and Kozo Saito, both from the University of Kentucky. What we report here is based on some experimental observations during that study and an additional experimental and numerical work conducted at the University of Kentucky.

During the pyrolysis experiments at FMR, we learned that samples used for the pyrolysis tests are crucial in obtaining repeatable and reliable results, thus increasing the importance of sample preparation. However, well-defined bench mark techniques for sample preparation have not been established. Differences in samples used by different researchers often causes uncertainties when test results are compared. An excellent review on the experimental methods in flame spread measurements by Fernandez-Pello and Hirano also points out this fact [5]. Establishment of a so-called bench mark sample can be a way to clarify experimental ambiguity and to develop a reliable and common

data base to study solid-phase heat transfer effects on pyrolysis and flammability tests. In the development of theoretical models for the pyrolysis/flammability of charring materials, the porosity of the samples, temperature dependent thermophysical properties, and radiant heat transfer into the sample must be accounted to accurately describe heat transfer in the solid phase [6]. In the case of certain non-charring materials such as PMMA, the effects of in-depth radiation absorption through the sample surface must be considered while developing theoretical models which predict pyrolysis and flammability processes [7].

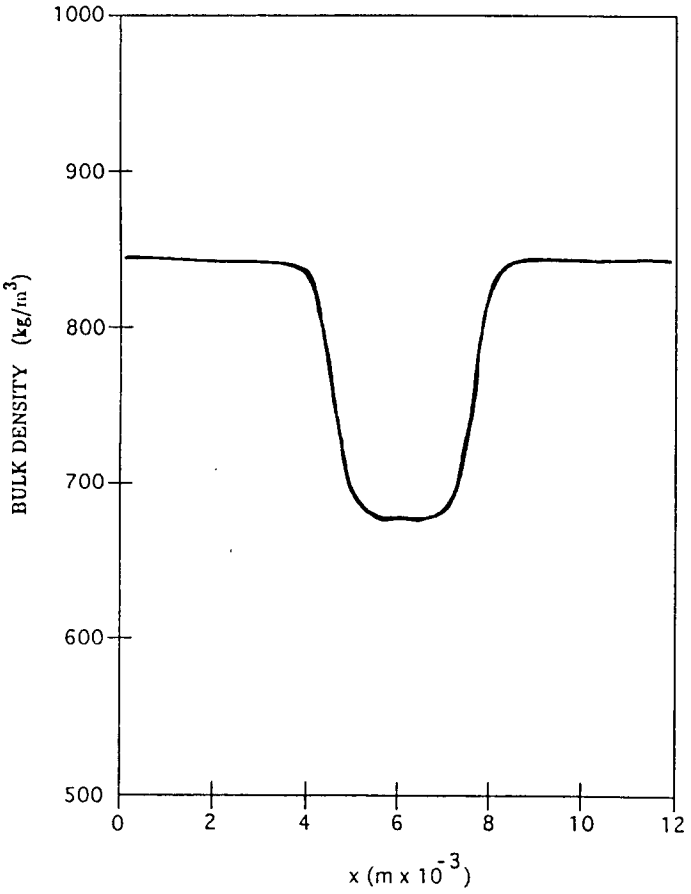

Figure 1. Density distribution of DFPB sample across its thickness.

In this paper we discuss: (1) the possible use of cellulose as a bench mark sample for pyrolysis and flammability tests, (2) the use of an effective thermal conductivity for charring materials such as wood and particle board, and (3) evaluation of in-depth radiation absorption effects in PMMA.

CELLULOSE SAMPLES

Wood and wood products (e.g. particle board) have been used for pyrolysis and flammability tests. As several researchers [3,8,9] have pointed out, inhomogeneity of natural woods complicates the task of obtaining reliable and reproducible data for these materials. Furthermore, the chemical and physical structure of the grain and porosity of the wood changes with the age of the wood by "aging" effect. To eliminate the effects of inhomogeneity of natural woods, DFPB is often used since it retains the general pyrolysis and combustion characteristics of natural woods, yet exhibits more uniform physical and thermal properties [8,10]. However, particle board has a significant density distribution across its thickness, as shown in Figure 1, which results from its manufacturing process. Particle board contains an organic binder (5 to 10% of the total weight) to hold the wood chips together, and which may affect the flammability data.

In order to test the binder effect, the particle board and solid wood (Douglas fir) samples were stored in a convection oven up to a forty day period under two different temperatures; 108°C and 130°C. These temperatures were selected since a temperature above 100°C is required to obtain a bone-dry sample. The dry sample has been used to eliminate effects associated with chemical reactions, water vapor and heat transfer processes due to liquid water in the porous structure of the above samples [11]. The mass of each sample was measured every 24 hours using an electronic balance with ± 1 mg accuracy. Figure 2 shows fraction of mass lost as a function of time after the samples were stored in the oven. The particle boards exhibited a continuous mass loss at 108°C and 130°C, while the solid Douglas fir did not exhibit any significant mass loss at a temperature of 108°C after the first 24 hours. A careful examination of the particle board samples treated in the oven for 24 hours was made under an optical microscope with eight times magnification; the samples developed small cracks on the surface indicating decomposition and evaporation of the binder material which was not evident in the solid wood Douglas fir sample. Therefore the binder efects must be accounted for when the particle boards are condi-

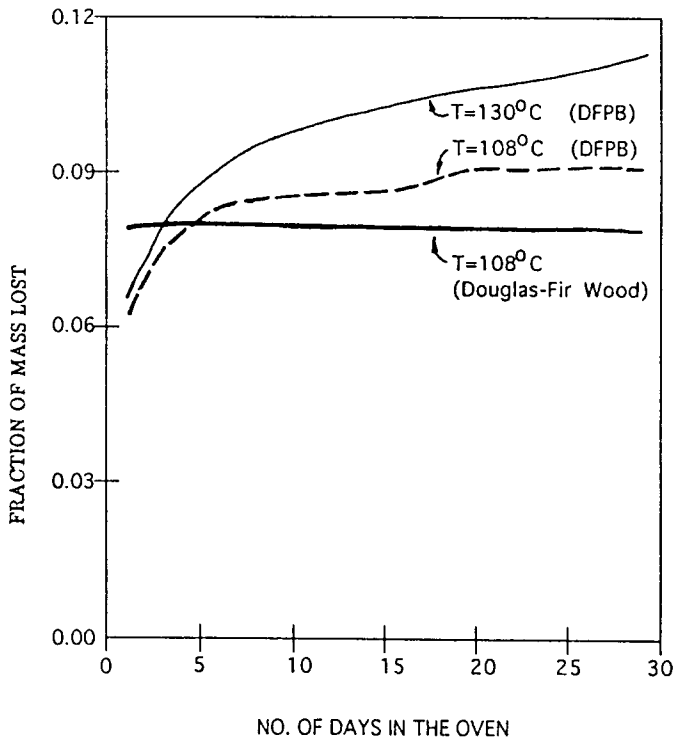

Figure 2. Mass loss vs. no. of days in the oven for DFPB and solid Douglas fir wood.

tioned at high temperatures. In addition, during pyrolysis tests both DFPB and solid wood Douglas fir samples exhibited a number of deep and randomly oriented surface cracks which affect the pyrolysis process [12]. However in this context, cellulose samples proved to be homogeneous in structure, of uniform density, and did not exhibit any surface cracks during pyrolysis tests. Surface photographs were taken for the cellulose and the solid wood Douglas fir samples, both exposed under a 60 kW/m² quartz heat flux and shown in Figure 3.

A simple apparatus, similar to that used by Sibulkin et al. [13] who studied flame retardation effects of materials, was designed to make cellulose samples of 12 cm diameter and 2.0 cm thickness with uniform density (schematic of the apparatus is shown in Figure 4). Three parts by weight of pure cellulose (20 micron particle size) to one part by weight of Whatman No. 40 ashless filter paper was soaked in distilled

Figure 3. *Photographs of surface structure for a cellulose sample (above) and a solid wood Douglas fir sample (below), both under 60 kW/m² quartz heat flux in a 100% nitrogen atmosphere.*

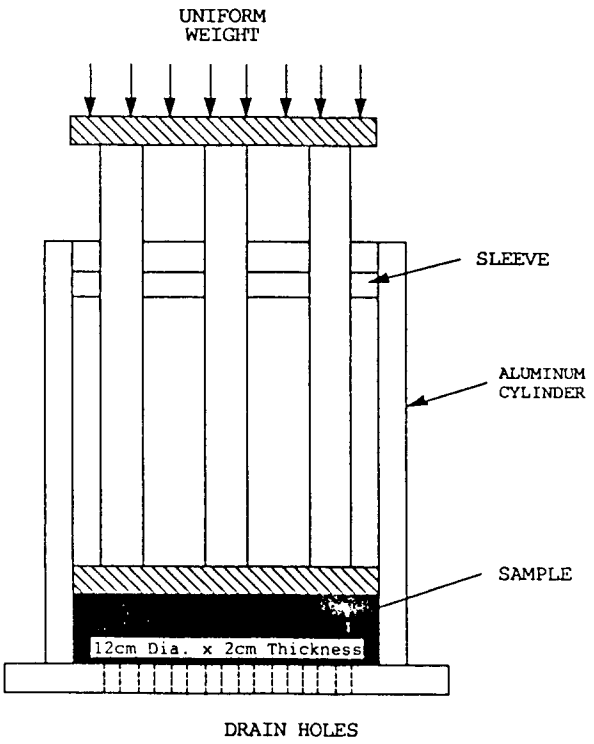

Figure 4. Schematic of the apparatus to make cellulose samples.

water and pulverized into a fine paste by a blender. A slurry of water and cellulose paste was pressed in the apparatus for eight hours which was long enough to cast the sample. A six kilogram weight was applied on the slurry for the first one hour period. The weight was increased approximately by 1 kg every hour, so that at the end of eight hours a total of 13 kg weight was uniformly applied on the surface of the 12 cm diameter sample. Exploratory tests showed that when a constant weight was applied to the slurry, air bubbles were trapped creating cavities in the final sample. At the end of the eight hour period the sample was removed from the apparatus and dried in an oven for at least 36 hours at 60°C (when the samples were dried at a temperature higher than 60°C, color of the samples changed to light brown indicating pyrolysis). The samples were sliced along several of its radii; the cross section was found to be very uniform under an optical microscope. Weight and volume of each sample was measured, and the density of the samples

was found to be 520 kg/m³ ± 6%. To check the effect of reflectivity of the cellulose sample, a cellulose sample was black coated with Paint I explained in the *In-depth Radiation Absorption section.* A 60 kW/m² quartz heat flux was given to the coated and the uncoated cellulose sample and surface temperature was measured by a fine thermocouple. Both samples exhibited a similar temperature history. However, the black coated sample resulted in approximately 20% shorter preheat time compared to the uncoated one. After the preheat period, surface of the uncoated sample changed to black showing no difference in the temperature history between the two samples. Interestingly, both samples exhibited no cracks on the surface.

THERMAL CONDUCTIVITY

The solid phase heat transfer model proposed here assumes that the pyrolysis process begins when significant weight-loss of the sample first occurs. From our experiments we have observed that for any incident heat flux, weight-loss begins when the DFPB sample attains a temperature of about 300°C [8,11]. A typical example of the temperature and weight-loss history recorded during the experiment under an external radiant heat flux of $q''_{in} = 33.0$ kW/m² is shown in Figure 5 [12]. It is assumed that once pyrolysis begins heat transfer into the solid is affected by the chemical changes which include the formation of char and tar. Therefore, pre-pyrolysis was defined as the period when the surface temperature of the sample is less than 300°C.

It is well known that the thermal conductivity, κ for DFPB have been reported to be a linear function of temperature [14]. The use of an effective thermal conductivity for particle board and the cellulose samples have been suggested previously [12]. The equations, and boundary conditions that describe the process are:

$$\frac{\partial}{\partial x}\left(\kappa \frac{\partial T}{\partial x}\right) = \varrho c \frac{\partial T}{\partial t} \quad 0 \le x \le L \tag{1}$$

$$T(x,0) = T_i \tag{1.a}$$

$$-\kappa \frac{\partial T(0,t)}{\partial x} = q''_{net} = q''_{in} - \epsilon\sigma T^4(0,t) \tag{1.b}$$

$$\frac{\partial T(L,t)}{\partial x} = 0 \tag{1.c}$$

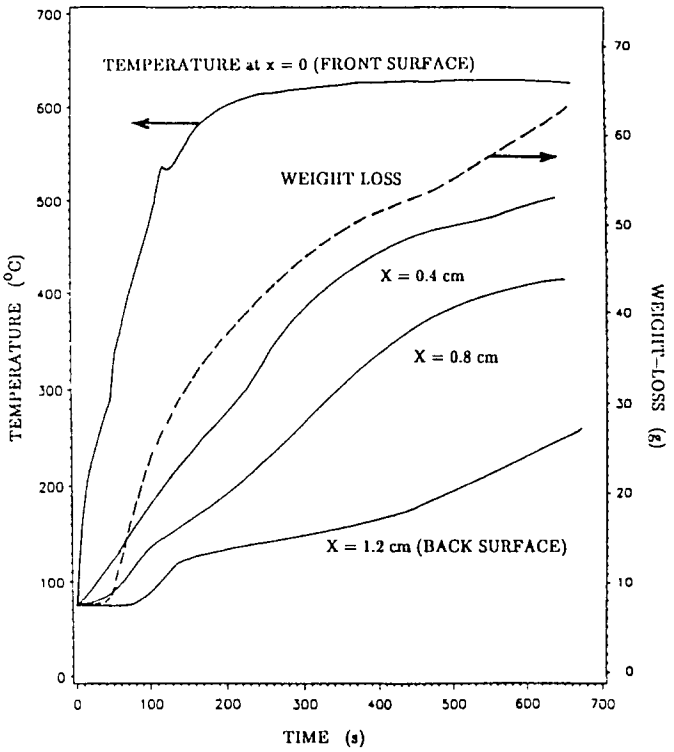

Figure 5. Temperature and weight-loss history of DFPB sample subject to $q''_{in} = 33.0\ kw/m^2$.

Where, x is normal to the sample surface, and positive in the direction of the sample thickness, T is the sample temperature, t is the time from the instant when the sample surface is exposed to the radiant heat flux, ϱ is the average density of the sample, T_i is the initial temperature of the sample, q''_{in} is the incident radiant heat flux, ϵ is the emissivity of the sample surface, σ is the Stefan-Boltzmann constant, and L is the sample thickness. Since DFPB has a density variation across the thickness as shown in Figure 1, the average density of DFPD is used.

Equation (1) is a non-linear one-dimensional heat diffusion equation, if the thermophysical properties are temperature dependent. Earlier we studied solutions of Equation (1) for three different cases [12]: for case I both $\varkappa$ and c are constant, for case II $\varkappa$ and c are linear functions of temperature, and for case III radiation penetration is included in $\varkappa$

as an additional term. When the DFPB sample is subject fire level incident heat flux values (20 to 40 kW/m²), radiant heat penetrates into the DFPB because of its porous structure. One way to model this effect is to add the radiative heat transfer term to Equation (1). However this adds unknown parameters. A second method is to define an effective thermal conductivity which includes radiation contribution. The effective thermal conductivity is defined as $\kappa = \kappa_s(T) + \kappa_R(T^3)$, where $\kappa_s(T)$ is the thermal conductivity of the solid and $\kappa_R(T^3)$ is an effective radiation contribution. Equation (1) was solved numerically for all three cases [12]. Numerical results showed that the best agreement with the experimental results for Case III, except when the surface temperature exceeded 300°C and pyrolysis occurred (see Figure 6).

Temperature distributions in the cellulose sample during a pyrolysis

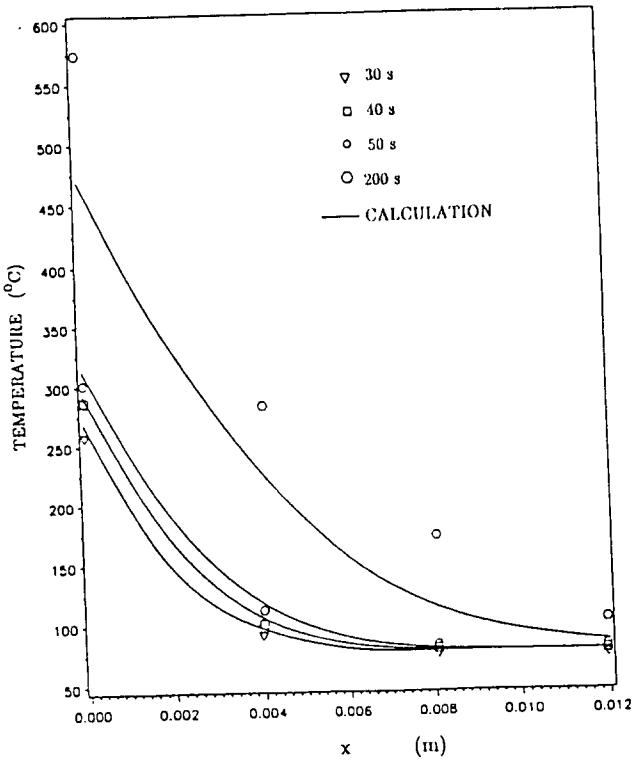

Figure 6. Experimental and calculated temperature distributions for DFPB sample subject to $q''_{in} = 33.0$ *kw/m².*

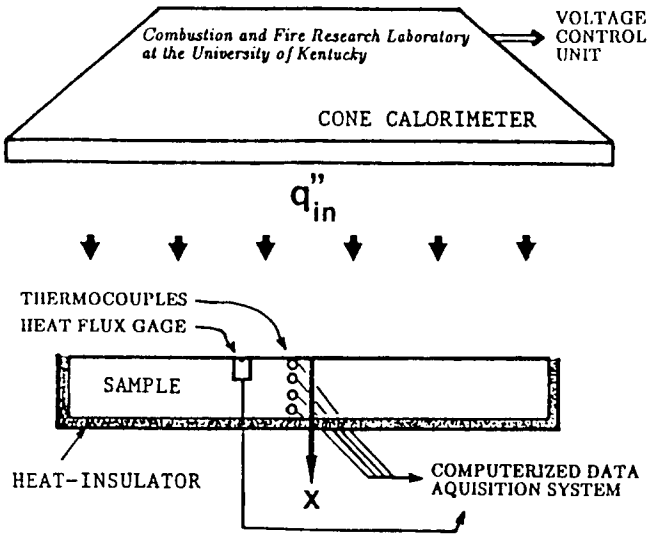

Figure 7. Schematic of experimental set up for pyrolysis tests.

test were measured by placing 100 μm diameter Alumel-Chromel thermocouples at the front and back surface of the sample and at four intermediate depths. The sample was cut into half across its thickness and fine holes were drilled normal to the cut at points where the thermocouples junctions were to be placed. After placing the thermocouple junctions, the holes were tightly packed with cellulose powder to ensure good contact between the thermocouple junction and the cellulose sample. The sample was glued together using a small amount of organic binder. In order to eliminate any effects due to cutting and the binder, the thermocouple junctions were located away from the surface of the cut. Temperature distributions were obtained for four different heat flux values (10,20,30, and 50 kW/m^2) at various times. In contrast to the pyrolysis tests on DFPB which were performed in a nitrogen atmosphere, the cellulose pyrolysis tests were performed in air. However, in the pre-pyrolysis period the effect of air on the temperature gradient is not dominant and the temperature distribution in the sample may not be significantly different from tests in a nitrogen atmosphere. The external radiant heat flux was provided by a Cone Calorimeter developed and extensively applied for flammability tests by Babrauskas [15,16].

Our DFPB model [13] was applied to the cellulose samples with the

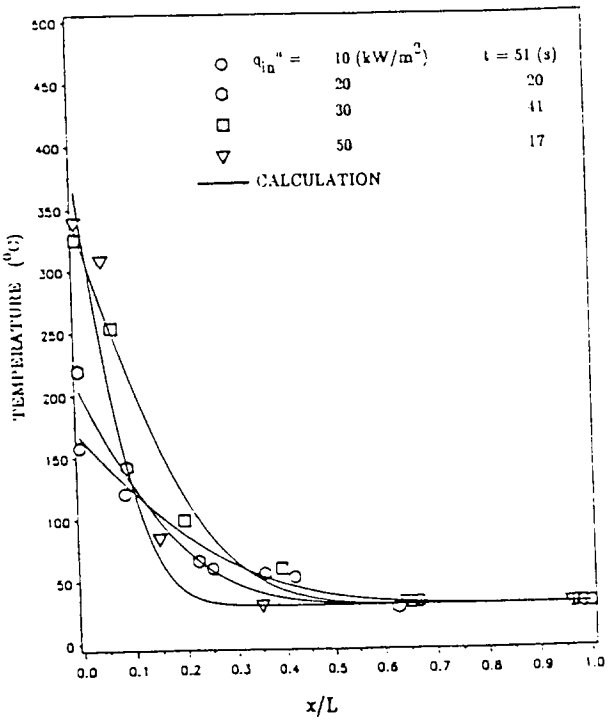

Figure 8. Experimental and calculated temperature distributions for cellulose samples subjected to four different heat fluxes.

thermal conductivity $= \kappa_s(T) + \kappa_R(T^3)$. Figure 8 shows representative results of the experimental and calculated temperature distributions for the four different heat flux values mentioned earlier. Table 1 presents a summary of the thermal properties used to solve Equation (1) for DFPB and cellulose samples.

Table 1. Thermophysical properties of DFPB and cellulose.

Material Type	Specific Heat c[kJ/kg K]	Thermal Conductivity κ[kW/mK]
DFPB	$0.594 + 0.0397T$	$1.53 \times 10^{-4} + 8.43 \times 10^{-8}T + 3.26 \times 10^{-13}T^3$
Cellulose	$0.7632 + 5.11 \times 10^{-3}T$	$4.82 \times 10^{-5} + 3.40 \times 10^{-7}T + 1.06 \times 10^{-13}T^3$

IN-DEPTH RADIATION ABSORPTION

During pyrolysis experiments with transparent and black PMMA, the formation of bubbles on the surface and at in-depth locations was observed. The formation of the bubbles below the surface may be attributed to in-depth radiation absorption by the PMMA sample. To avoid the effect of in-depth radiation absorption during pyrolysis tests, black PMMA was used instead of transparent PMMA; however, it also formed bubbles at in-depth locations. To further reduce in-depth radiation absorption, the sample surface was coated with three different types of black paints. Paint I is a commercially available acrylic non-luster paint, paint II is a commercially available thermal resistance paint (silicone based) and paint III is a mixture of approximately 60% liquid acrylic and 40% lamp black by volume. Black PMMA samples of 12 cm diameter and 2.4 cm thickness were cut from a sheet. Paints I and II were uniformly sprayed on the sample surface. After several practices, we were capable of making a uniform coating of 50 to 60 μm thickness on the sample surface using a special coating device.

To estimate effects of in-depth radiation absorption, external radiant heat flux values ranging from 30 kW/m^2 to 150 kW/m^2 (covers fire level heat fluxes) were uniformly applied to the sample surface for two minutes. After the samples cooled down, they were cut into half across the thickness. The sample cross section area which is normal to the exposed surface was polished so that the penetration depth of the bubble could be clearly identified. Optical microscope photographs (eight times magnification) across the sample thickness enabled to estimate the bubble penetration depth. Figure 9 shows the sample surface and cross section with and without coating by paint III after being exposed to a heat flux of 30 kW/m^2.

The average bubble penetration depth of the samples coated with paint I and paint III showed no difference, while the samples coated with paint II clearly exhibited deposition of silicon on the sample surface affecting the PMMA's thermal response time, therefore resulting in a delay in the pyrolysis time. The bubble formation depth is more for the lower heat flux, probably due to the slower pyrolysis rate and smaller temperature gradients. The lower heat flux created soft and large shiny bubbles on the sample surface through which radiation is likely to penetrate. Bubble formation depth for higher heat flux values was smaller probably due to the presence of very steep temperature gradients near the surface. The surface of the samples subjected to the higher heat flux values developed smaller size bubbles, which were hard and dull in texture.

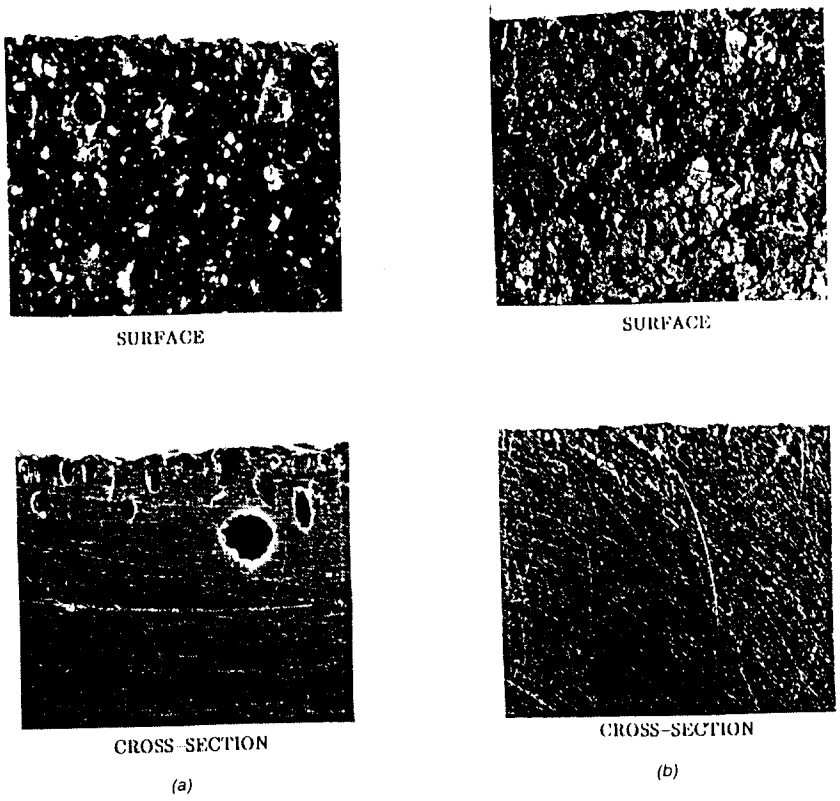

Figure 9. Eight times magnification optical microscope photographs of Black PMMA sample surface and cross-section subjected to an external radiant heat flux of 30.0 kW/m²: (a) uncoated and (b) coated.

Radiant heat exposure tests were conducted on coated and uncoated transparent PMMA. The exposure tests on transparent PMMA were conducted in an atmosphere of air. The transparent PMMA samples were exposed to radiant heat flux values up to 70 kW/m². The coated samples exhibited smaller bubble formation depths as compared to the uncoated samples, similar to the Black PMMA results. Figure 10 shows the relationship between the bubble formation depth and the incident radiant heat flux, for uncoated and coated, black and transparent PMMA. Thompson and Drysdale [17] also studied a bubble layer depth as a function of external radiant heat flux and found that it decreased with increasing the radiant heat flux in agreement with our results.

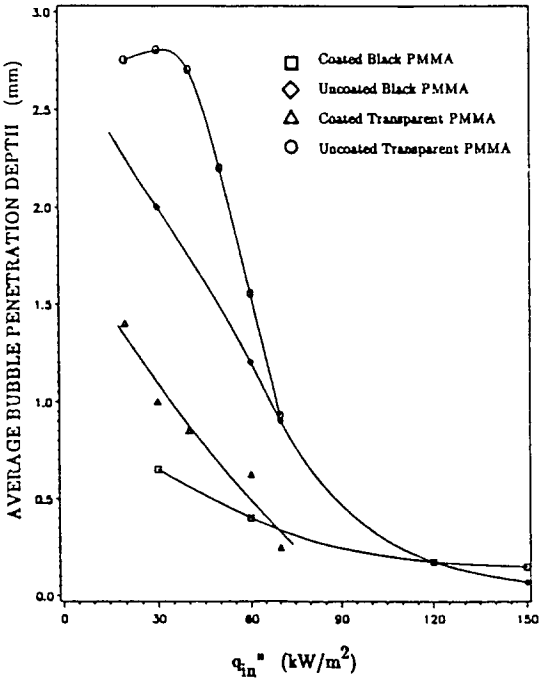

Figure 10. Average bubble penetration depth vs. heat flux for coated and uncoated, black and transparent PMMA (exposure time, 2 min).

The absorption coefficient for transparent PMMA for 633 nm is $5 \times 10^{-5}m^{-1}$, and for 400 nm is $1 \times 10^{-4}m^{-1}$, indicating the importance of in-depth radiation absorption [18]. Our studies on the effect of in-depth radiation also clearly indicate that heat radiation absorption must be given serious consideration in heat transfer models for materials like PMMA. However, there is no established correlation for the bubble penetration depth and in-depth radiation [19], although some qualitative studies were conducted by Thompson and Drysdale [17]. Heat losses due to convection and reradiation from the sample surface may contribute to bubble formation, but these losses are approximately same for both coated and uncoated surfaces in our experiments. Therefore, a correlation between the bubble penetration depth and in-depth radiation absorption is likely to exist since our experiments have proved that by decreasing in-depth radiation absorption (using surface coated samples), the bubble penetration depth also

decreases. Further studies to accurately determine the relationship between the bubble formation and temperature distribution in coated and uncoated samples are needed.

SUMMARY AND CONCLUSIONS

1. The use of cellulose samples as a bench mark material for pyrolysis and flammability studies is suggested. Unlike natural wood and particle board, the cellulose sample is physically homogeneous. Since cellulose constitutes a large percentage of wood, pyrolysis of cellulose is representative of pyrolysis of wood. A simple method to manufacture cellulose samples is established. Under controlled experimental conditions the cellulose sample pyrolyzes more uniformly than particle board which develops surface and in-depth cracks. The importance of well controlled drying of samples (DFPB, wood, and cellulose) before pyrolysis tests is stressed upon, especially in the case of DFPB where binder effects are prominent.
2. An effective thermal conductivity $\kappa = \kappa_s(T) + \kappa_R(T^3)$ is the solid thermal conductivity and $\kappa_R(T^3)$ is the radiation contribution term, is suggested for use when modeling heat transfer in materials such as the DFPB and cellulose samples. Experimental and calculated temperature distributions agree well when the effective thermal conductivity is employed.
3. When PMMA samples are subjected to external radiant heat flux values, bubble formation on the surface and at in-depth locations is observed. The depth of the bubbles depends on the incident radiant heat flux. The bubble penetration depth was considerably reduced when the PMMA samples (black and transparent) were coated (50 μm thickness) with black paint (lamp black) in order to decrease the in-depth absorption of the radiant heat flux and increase surface absorption. It is likely that the temperature gradients and consequently the heat transfer process in the sample is affected by in-depth radiation absorption. Work is needed to further determine the effects of in-depth radiation on heat transfer in the solid.

ACKNOWLEDGEMENTS

We would like to thank Ron Alpert, Mike Delichatsios and John deRis for their guidance and a series of stimulating discussions when S. V. and K. S. were involved in a FMR fire research program. This work

is in part supported from the National Institute of Standards and Technology under Grant #60NANB9D0960, and in part from the Center for Robotics and Manufacturing Systems, University of Kentucky under the visiting scholar's fellowship program.

REFERENCES

1. Delichatsios, M. M., T. H. Panagiotou and F. Kiley. 1991. *Combustion and Flame,* 86:323–332.
2. Delichatsios, M. M. and M. A. Delichatsios. 1993. *Combustion and Flame,* 89:5–16.
3. Kashiwagi, T., T. J. Ohlemiller and K. Werner. *Combustion and Flame,* 69:331–345.
4. Kashiwagi, T. and H. Nambu. 1992. *Combustion and Flame,* 88:345–368.
5. Fernandez-Pello, A. C. and T. Hirano. 1983. *Combustion Science and Technology,* 32:1–31.
6. Williams, F. A. 1985. *Combustion Theory, Benjamin Cummings, 2nd Edition.*
7. Delichatsios, M. and K. Saito. 1991. *Fire Safety Science–Proceedings of the Third International Symposium,* Elsevier Applied Science, pp. 217–226.
8. Saito, K., F. A. Williams, I. S. Wichman and J. G. Quintiere. 1989. *J. Heat Transfer,* 111:438–445.
9. Wichman, I. S. and A. Atreya. 1987. *Combustion and Flame,* 68:231–247.
10. Quintiere, J., M. Harkleroad and Y. Hasemi. 1986. *Combustion Science and Technology,* 48:191–222.
11. Shafizadeh, F. 1984. Chemistry of Wood, Publication of the American Chemical Society.
12. Parker, W. J. 1985. "Development of a Model for the Heat Release Rate of Wood–A Status Report," *NBSIR85-3163,* Gaithersburg, MD: National Institute of Standards and Technology.
13. Sibulkin, M. and S. S. Tewari. 1985. *Combustion and Flame,* 59:31–42.
14. Venkatesh, S. and K. Saito. 1990. *Thermal Conductivity 21, Proceedings of the Twenty-First International Conference on Thermal Conductivity,* C. J. Cremers and H. A. Fine, eds., Plenum, pp. 687–706.
15. Babrauskas, V. and W. J. Parker. 1986. "Ignitability Measurements With the Cone Calorimeter," *NBSIR 86-3445,* Gaithersburg, MD: National Institute of Standards and Technology.
16. Babrauskas, V. and U. Wickstrom. 1988. *Fire Safety Science–Proceedings of the 2nd International Symposium,* Hemisphere Publication Company, pp. 813–822.
17. Thompson, H. E. and D. D. Drysdal. 1987. *Fire and Materials,* 11:163–172.
18. 1963. *Handbook of Polymers, 2nd Edition,* J. Brandeyis, ed.
19. Kashiwagi, T. 1990. Personal Communications, National Institute of Standards and Technology.

BIOGRAPHIES

Dr. Masatoshi Daikoku

Dr. Daikoku holds Doctor of Engineering degree from Tohoku University and currently is an associate professor at Hachinohe Institute of Technology in Japan. His area of research interest includes spray and atomization, heat transfer, flow visualization, and combustion. Dr. Daikoku spent one year (1989 through 1990) at the University of Kentucky as a visiting scholar being involved in a flow visualization study on fire-induced flow along the vertical corner walls which was sponsored by the National Institute of Standards and Technology.

Dr. Shyam Venkatesh

Dr. Venkatesh holds Ph.D. degree from the University of Kentucky and currently is a senior staff engineer at Acurex Environmental Corporation. His area of research interest includes studies of pollutants and combustion by-products formation and control, chemical engineering, and computer simulation in heat and mass transfer process. Prior to joining the current company, he was a research associate at the Combustion and Fire Research Laboratory, and the Center for Applied Energy Research, both at the University of Kentucky.

Dr. Kozo Saito

Dr. Saito holds Doctor of Engineering degree from Seikei University and is currently a professor at the department of mechanical engineering of the University of Kentucky and serves as the director of Combustion and Fire Research Laboratory. Prior to joining the current institution, Dr. Saito was at the University of California, San Diego as a postdoctoral, Princeton University as professional research staff, and intergovernmental personnel act at the National Institute of Standards and Technology. His area of research interest includes experimental combustion, fire research and creativity study.